

OFFICE OF NAVAL RESEARCH  
END-OF-THE-YEAR REPORT  
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT: N00014-94-1-0703

Solution- and Solid-state Photoelectrochromic Switching in Organized Assemblies

Chad A. Mirkin

Northwestern University  
Department of Chemistry  
Evanston, IL 60208-3113

July 7, 1997



OTIC QUALITY INSPECTED 3

19970711 047

OFFICE OF NAVAL RESEARCH  
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

PR Number:

Grant Number: N00014-94-1-0703

Grant Title: Solution- and Solid-state Photoelectrochromic Switching in Organized Assemblies

Principal Investigator: Chad A. Mirkin

Mailing Address: Department of Chemistry, Northwestern University, Evanston, IL 60208-3113

Phone Number: 847-491-2907

Fax Number: 847-491-7713

E-mail Address: CAMirkin@chem.nwu.edu

http address: <http://www.chem.nwu.edu/~mkngpr>

A. + Number of papers submitted to refereed journals, but not published: 4

B. + Number of papers published in refereed journals (listed below): 8

C. + Number of books or chapters submitted, but not yet published: 0

D. + Number of books or chapters published: 0

E. + Number of printed technical reports/non-refereed papers (listed below): 5

F. + Number of patents filed (below listed): 1

G. + Number of patents granted: 0

H. + Number of invited presentations (below listed): 20

I. + Number of submitted presentations (below listed): 0

J. + Honors/Awards/Prizes for contract/grant employees (below listed): 3

Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this PR number (below listed): 3

Graduate Students: 3

Post-Doctoral Associates:

Female Graduate Students: 0

Female Post-Doctoral Associates: 0

Minority\* Graduate Students: 0

Minority\* Post-Doctoral Associates: 0

Asian Graduate Students: 1

Asian Post-Doctoral Associates: 0

Minority Undergraduate Students: 0

A. Number of papers submitted to refereed journals, but not published: 4

1. Elghanian, J. J. Storhoff, R. C. Mucic, Letsinger, R. L.; Mirkin, C. A. "Colorimetric DNA-Detection," *Science*, 1997, in press.

2. Covington, M.; April, M. M.; Paraonon, E.; Greene, L. H.; Xu, F.; Zhu, J.; Mirkin, C. A. "Observation of Surface-induced Broken Time-reversal Symmetry in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> Tunnel Junctions", *Phys. Rev. Lett.* 1997, in press.

3. Piner, R. D.; Mirkin, C. A. "Effect of water on lateral force microscopy in air," *Surface Science Letters*, 1997, submitted.

4. Campbell, D. J.; Mirkin, C. A. "Solvent-Dependent PhotoDiodes Prepared From SAMs of Azobenzene Alkanethiols," *J. Phys. Chem.* **1997**, submitted.

Number of papers published in refereed journals (for each, provide a complete citation): 8

1. Storhoff, J. J.; Mucic, R. C.; Mirkin, C. A. "Strategies for Organizing Nanoparticles into Aggregate Structures and Functional Materials," *Journal of Cluster Science*, **1997**, *8*, 179-216

2. Mirkin, C. A.; Xu, F.; Zhu, J. "Controlling the Surface Properties of High Temperature Superconductors," *Adv. Mater.*, **1997**, *9*, 167-173.

3. Chen, K.; Xu, F.; Mirkin, C. A.; Lo, R. K.; Nanjundaswamy, K. S.; Zhou, J.; McDevitt, J. T. "Do Alkanethiols Adsorb onto the Surfaces of Tl-Ba-Ca-Cu-O-Based High Temperature Superconductors? The Critical Role of H<sub>2</sub>O Content on the Adsorption Process," *Langmuir*, **1996**, *12*, 2622-2624.

4. Lo, R.-K.; Zhou, J.; Zhao, J.; McDevitt, J. T.; Xu, F.; Mirkin, C. A. "Polypyrrole Growth on YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> Modified with a Self-assembled Monolayer of N-(3-aminopropyl) Pyrrole: Hardwiring the Electronic Hot Spots on a Superconductor," *J. Am. Chem. Soc.*, **1996**, *118*, 11295-11296.

5. Campbell, D.; Herr, B. R.; Hulteen, J. C.; Van Duyne, R. P.; Mirkin, C. A. "Ion-gated Electron Transfer in Self-assembled Monolayer Films," *J. Am. Chem. Soc.*, **1996**, *118*, 10211-10219.

6. Mirkin, C. A.; Letsinger, R. L.; Mucic, R. C.; Storhoff, J. J. "A DNA-Based Method for Rationally Organizing Nanoparticles into Macroscopic Materials," *Nature*, **1996**, *382*, 607-609.

7. Zhu, J.; Xu, F.; Schofer, S. J.; Mirkin, C. A. "The First Raman Spectrum of an Organic Monolayer on a High Temperature Superconductor: Direct Spectroscopic Evidence for a Chemical Interaction between an Amine and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>," *J. Am. Chem. Soc.*, **1997**, *119*, 235-236.

8. McDevitt, J. T.; Ritchie, J. E.; Clevenger, M. B.; Lo, R.-K.; Mirkin, C. A.; Xu, F. "Molecular Engineering of Organic Conductor/High-T<sub>c</sub> Superconductor Assemblies," *Synthetic Metals*, **1997**, *84*, 407-408.

Number of printed technical reports/non-refereed papers (listed below): 5

1. Covington, M.; Xu, F.; Mirkin, C. A.; Feldmann, W. L.; Greene, L. H. "Tunneling Spectroscopy of Superconducting Y<sub>1-x</sub>Pr<sub>x</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> Thin Films," *Czech. J. Phys.* **1996**, *46*, 1341-1342.

2. Caldwell, W. B.; Mirkin, C. A. "The Design And Synthesis of "Rotoball": A New Strategy For Preparing Highly Ordered Fullerene-Based Monolayer Films," *Proceedings of the Electrochemical Society*, **1996**.

3. Xu, F.; Chen, K.; Zhu, J.; Campbell, D. J.; Mirkin, C. A.; Lo, R.; Zhao, J.; McDevitt, J. T. "Probing The Surface Coordination Chemistry of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>," *Proceedings of the Electrochemical Society*, **1996**.

4. Mirkin, C. A. Review of *Electron Transfer and Radical Processes in Transition Metal Chemistry*, D. Astruc, in *Angew. Chem., Int. Ed. Engl.*, in press.

5. Mirkin, C. A.; Ratner, M. A. "Self-assembled Monolayers and Superlattices", *Encyclopedia Britannica*, in press.

Number of invited presentations: 20

1. Washington University, St. Louis, MO: **Colloquium**, "Redox-active Hemilabile Ligands: from Molecules to Materials" (1996)

2. DuPont Chemical Company, Deepwater, NJ: "New Natural and Synthetic Building Blocks for Two and Three-Dimensional Supramolecular Assemblies" (1996)

3. Purdue University, West Lafayette, IN: "New Natural and Synthetic Building Blocks for Two and Three-Dimensional Supramolecular Assemblies" (1996)

4. University of Illinois, Champaign-Urbana "New Natural and Synthetic Building Blocks for Two and Three-Dimensional Supramolecular Assemblies" (1996)

5. Pennsylvania State University, University Park, PA: "New Natural and Synthetic Building Blocks for Two and Three-Dimensional Supramolecular Assemblies" (1996)

6. Indiana University-Purdue at Indianapolis, IN: "New Natural and Synthetic Building Blocks for Two and Three-Dimensional Supramolecular Assemblies" (1996)

7. **Gordon Research Conference** on Electrochemistry, Ventura, CA: "Redox-active Hemilabile ligands: from Molecules to Materials" (1996)

8. **Rank Charities Lectures** on Optical Composites: Grasmere, England: "New Building Blocks for Self-Assembled Functional Materials" (1997)

9. NSF Workshop on Materials, Philadelphia, PA: "New Building Blocks for Self-Assembled Functional Materials" (1997)

10. Florida Conference on Advanced Materials, Gainesville, FL: "New Building Blocks for Self-Assembled Functional Materials" (1997)

11. Georgia Institute of Technology, Atlanta, GA: "New Building Blocks for Self-Assembled Functional Materials" (1997)

12. **Gordon Research Conference** on Thin Films, Newport, RI: "New Building Blocks for Self-Assembled Functional Materials" (1997)

13. **Gordon Research Conference** on Inorganic Chemistry, Newport, RI: "Redox-active Hemilabile

Ligands: from Molecules to Materials" (1997)

14. Korean Institute of Science and Technology, Seoul, Korea: "New Building Blocks for Self-Assembled Functional Materials" (1997)

15. Institute of Chemistry, Academia Sinica, Taipei, Taiwan: "New Building Blocks for Self-Assembled Functional Materials" (1997)

16. National Taiwan University, Taipei, Taiwan: "New Building Blocks for Self-Assembled Functional Materials" (1997)

17. Lucent Technology, Murray Hill, NJ: "New Building Blocks for Self-Assembled Functional Materials" (1997)

18. National Tsing Hua University, Tsing Hua, Taiwan: "New Building Blocks for Self-Assembled Functional Materials" (1997)

19. Pohang University, Pohang, Korea: "New Building Blocks for Self-Assembled Functional Materials" (1997)

20. **Gordon Research Conference** on Thin Film, Newport, RI: "New Building Blocks for Self-Assembled Functional Materials" (1997)

J. Honors/Awards/Prizes for contract/grant employees:

DuPont Young Professor Award (continuation)

Camille Dreyfus Teacher-Scholar Award (continuation)

Promoted to "Full" Professor

Promoted to Charles E. and Emma H. Morrison Professor of Chemistry, effective Sept. 1, 1997

## Part II

A. PI: Chad A. Mirkin

B. Telephone number: 847-491-2907

C. ONR Scientific Officer: Dr. John C. Pazik

D. Description of Project: The goal of the project is to prepare, characterize, and study organized, densely packed, highly oriented monolayer structures of redox- and photoactive adsorbate molecules (azobenzenes and ferrocenylazobenzenes) on a variety of conducting substrates. These types of molecular assemblies are relevant to the development of new forms of ultrahigh density optical data storage media, chemical sensors, optical switches, and photon counters. An understanding of the chemical and physical processes that can occur within such assemblies is critical to the development of such high performance optical materials. The specific aim of the project is to examine the role of film structure on ion transport, electron transfer, and photochemical reactions that occur in self-assembled monolayer films (SAMs). Two of the primary tools used for film characterization are state-of-the art "molecular resolution" atomic force microscopy and synchrotron x-ray methods (diffraction and standing wave).

E. Significant results: In last year's progress report, we presented initial experiments that demonstrated the concept of a photodiode in the context of a self-assembled monolayer (SAM) of a ferrocenylazobenzenealkanethiol on Au(111). Over the course of the past year we have devoted significant effort to the characterization of this novel SAM device. The device consists of a ferrocenylazobenzenealkanethiol/azobenzenealkanethiol (1:99) SAM on Au(111) and a sacrificial source of electrons in the form of ferrocyanide. When the azobenzene groups in the SAM are photochemically converted from their *trans*- to *cis*- forms, the porosity of the film in H<sub>2</sub>O is decreased such that the ferrocyanide ions cannot access the Au electrode surface. This results in a situation where all electron transfer events between the ferrocyanide source molecules and the electrode surface must be mediated by the ferrocenylazobenzene groups. The process is thermodynamically forbidden in the reverse direction (i.e. the ferrocenylazobenzene cannot reduce ferricyanide to ferrocyanide). Therefore, this structure exhibits diode-like behavior or current rectification. In this state, the electrochemical response exhibits a large oxidative wave (i.e. the ferrocenylium groups can oxidize the ferrocyanide) with no detectable current associated with reduction. Note that the "source" molecule is critical. If ferrocene is used instead of ferrocyanide, normal electron transfer is observed because the smaller ferrocene molecules can penetrate the SAM and access the electrode surface. When the film is irradiated with the appropriate wavelength of light (~360 nm), it can be converted back to the porous film, and reductive current can once again be observed. This process is a unique form of amplification. In other words, a few photons can open up the film to allow an infinite number of electrons to pass from the source ferrocyanide ions to the electrode surface. This is not just a phenomenon associated with photochemistry. If a chemical reagent causes a structural change in the film a similar phenomenon can be observed. For example, ethanol introduces a structural change in the *cis*-film that increases its porosity and breaks down the diode behavior. This is an example of how a chemical sensor can be constructed from this type of device; a few molecules of analyte (e.g. ethanol) can bring about a structural change in the film that releases a virtually infinite number of electrons that can be measured easily in the form of electrical current. Motorola is currently evaluating this technology for sensor development.

In an offshoot of this YIP award, which will become the major focus of a renewal proposal, we have explored the use of SAM chemistry to modify high temperature superconductors. This was a joint venture between the McDevitt Group and our group, which was initiated by the 1995 ONR Program Review in Minnesota. This collaborative effort has resulted in: 1) new methods for passivating HTSCs for enhanced corrosion resistance, 2) a better understanding of polymer nucleation and growth on HTSC surfaces, 3) strategies for improving adhesion between polymeric materials and HTSCs, and 4) general methods for tailoring the surface and interfacial properties of HTSCs. Recently, we have shown in a collaboration with L. Greene at UIUC that we can prepare SIN junctions from these novel surface structures. This is a significant result since it could allow one to design tunnel junctions, and the many devices (SQUIDS, Logic Circuits, and IR detectors) derived from them, at the molecular level. Confidentiality and Materials Transfer agreements have been executed with Quantum Magnetics and Motorola. Finally, we have been able to prepare a new class of superconductor nanoparticles by etching superconductor powders from the micron to nanometer length scale. These nanoparticles form stable suspensions in organic media and could give entry into new class of highly processable superconductor materials.

F. Future plans. We are in the process of winding down the YIP award, and between now and October, we will conclude the characterization of the SAM-based diodes. We still need spectroscopic evidence for the structural transformations induced by solvent (e.g. ethanol). Here, we will utilize surface-enhanced Raman spectroscopy (SERS) to characterize the structures in air, water, and ethanol. The azobenzene groups are excellent Raman markers, and if solvent is being incorporated into the film, this should be apparent through a comparison between the Raman spectra for azobenzene dissolved in ethanol and the SAM in ethanol. We recently have constructed an AFM solution cell, which will allow us to analyze structural changes *in situ* as a function of external conditions (solvent, temperature, etc.).

In addition, we plan to fully characterize the nanoparticle superconductors (described above), which will become a major topic for our renewal effort. The surface and bulk compositions of these particles need to be experimentally determined. Stability, conductivity, and magnetic properties as a function of temperature also must be investigated. These materials are particularly attractive for use as the counter electrodes in the fabrication of SIS tunnel junction devices, an avenue which we will subsequently be pursuing.

G. Graduate Students and post-doctorals currently working on the project:

Dean Campbell - Graduate student  
Robert Mucic - Graduate Student  
Jin Zhu - Graduate Student



# SOLUTION AND SOLID-STATE PHOTOELECTROCHROMIC SWITCHING IN ORGANIZED ASSEMBLIES

Chad A. Mirkin, Professor, Northwestern University

## Technology Issues:

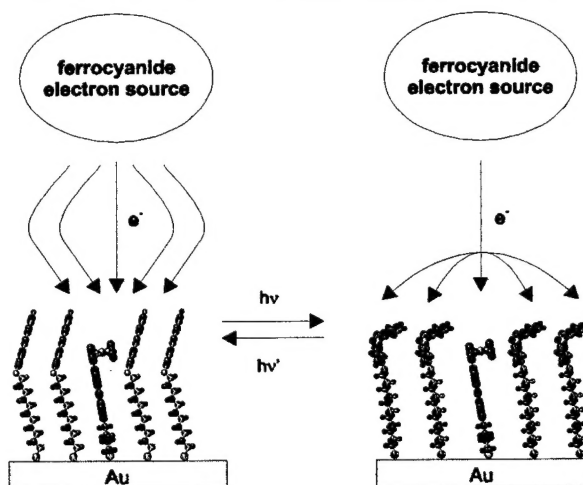
information storage media, ultra sensitive actinometers, chemically sensitive interfaces and devices, general nanofabrication procedures, and the development of new surface analytical methodology

## Objectives:

- Understand the relationship between structure and function in assemblies of photo-electrochromic materials
- Design and synthesize novel adsorbate molecules that form SAMs with distinct AFM and X-ray diffraction signatures that are useful in characterizing the monolayer self-assembly process on Au(111)
- Develop methods that can be used to characterize processes that occur in surface-confined nanoscale assemblies

## Approach:

- Utilize state-of-the-art AFM and synchrotron in-plane XRD methods to characterize the structures of photo- and electroactive assemblies on well-defined surfaces.
- Characterize photoinitiated and electron transfer processes in these novel assemblies by electrochemical methods and surface FTIR and Raman spectroscopies
- Develop an understanding of the relationship between SAM structure and function



## Accomplishments:

- Invented and developed the concepts of ion- and photon-gated electron transfer in SAMs
- Developed a photoswitchable molecular diode based on two-component SAMs of azobenzene and ferrocenyl-azobenzene adsorbate molecules; showed that such structures could behave as highly sensitive photon counters or chemical sensors
- Discovered that these structures are highly solvent dependent

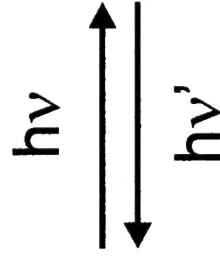
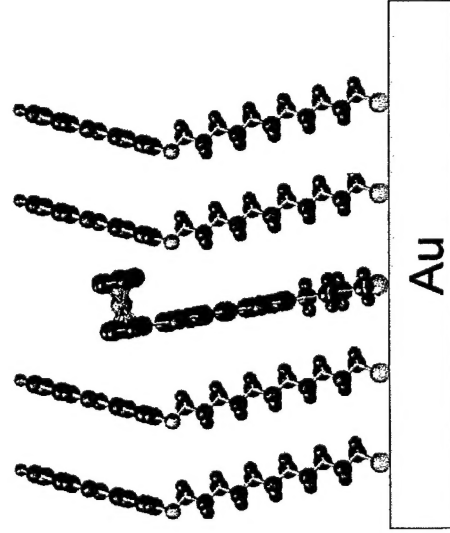
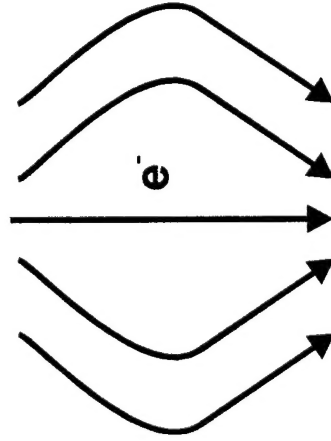
## Transitions:

- Active confidentiality and materials transfer agreements with Rohm and Haas, Motorola, and Quantum Magnetics
- A collaboration with L. Greene (UIUC) aimed at evaluating the use of SAMs for the preparation of SIN tunnel junctions
- A collaboration with J. T. McDevitt at UT, Austin focusing on developing SAM methods for controlling HTSC surface and interfacial properties

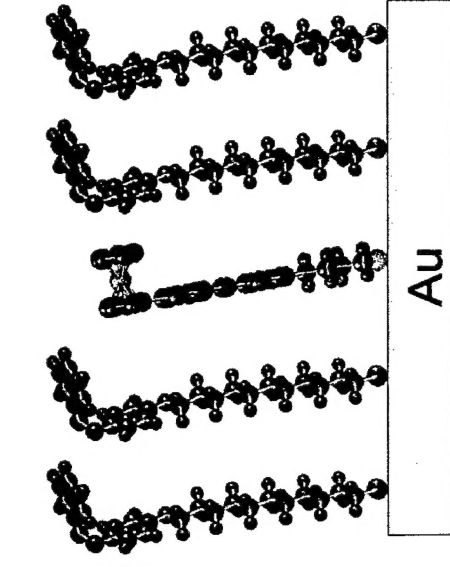
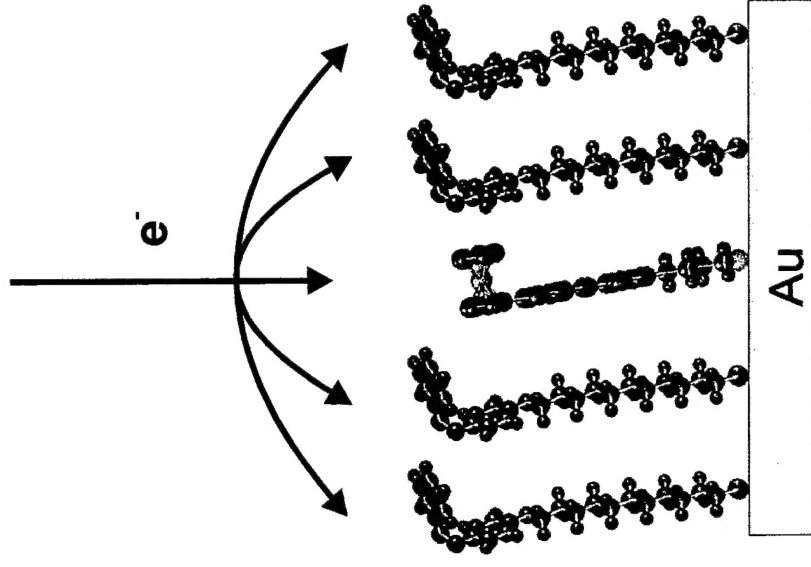


# Photon Gated Electron Transfer: A Photoswitchable SAM-based Diode

ferrocyanide  
electron source

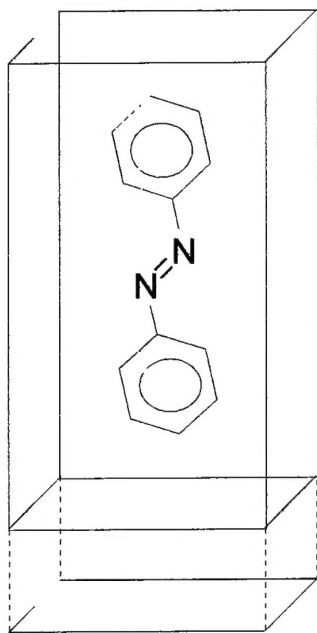


ferrocyanide  
electron source



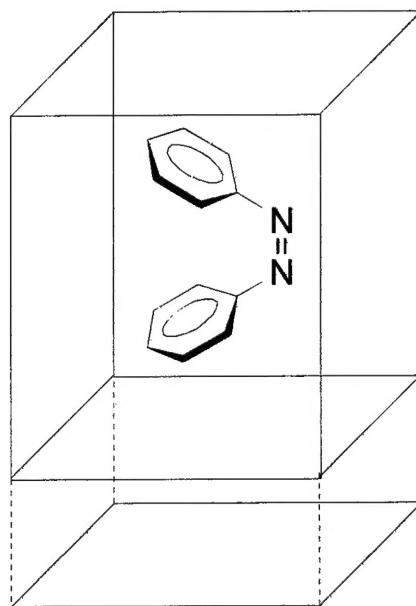
# Spatial Considerations of *trans* and *cis* Azobenzene Monolayers

Volume:  $247.8 \text{ \AA}^3$

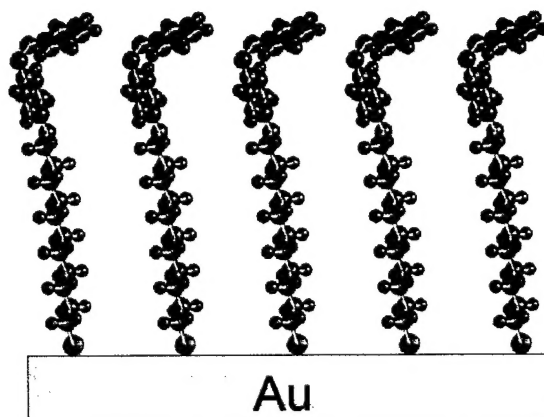
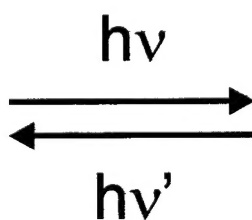
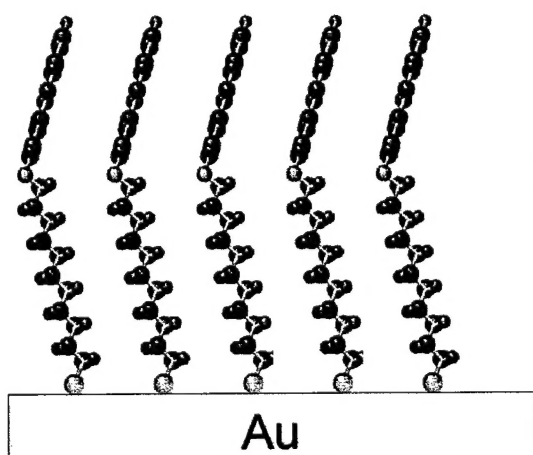


Area:  $35.2 \text{ \AA}^2$

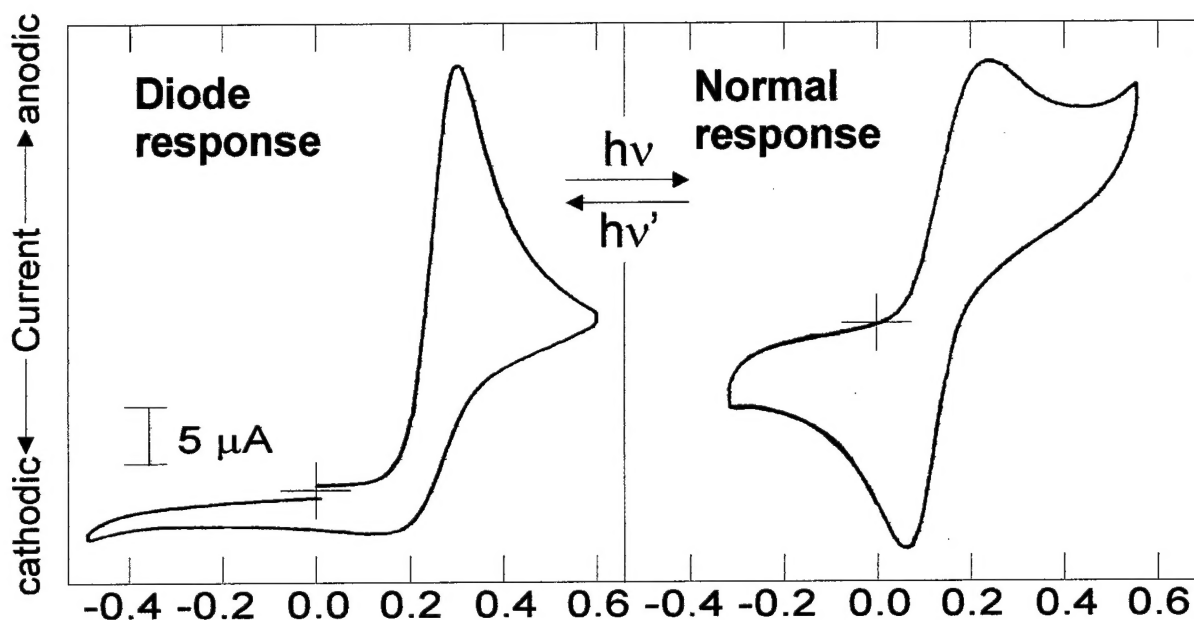
Volume:  $249.4 \text{ \AA}^3$



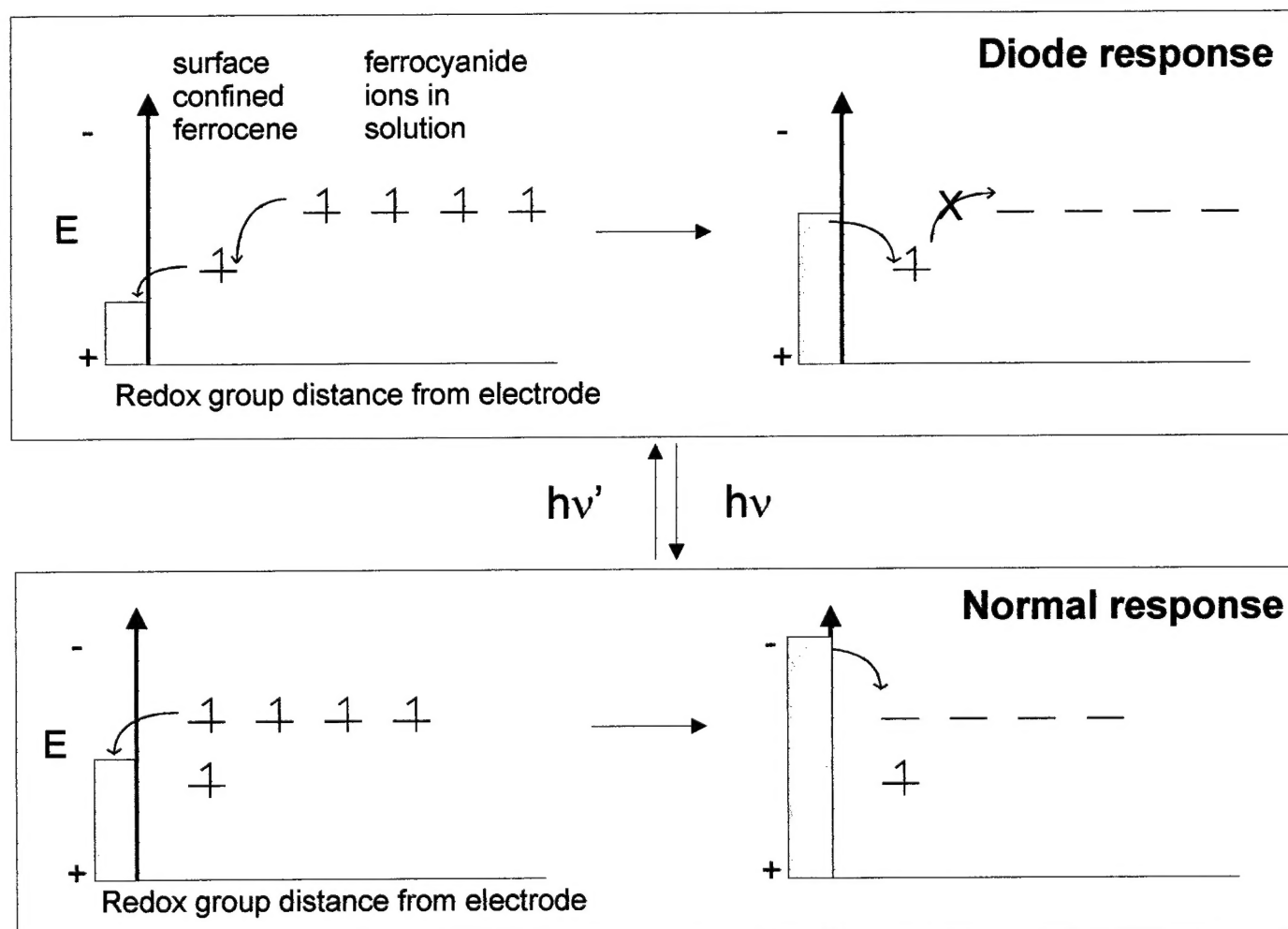
Area:  $65.8 \text{ \AA}^2$



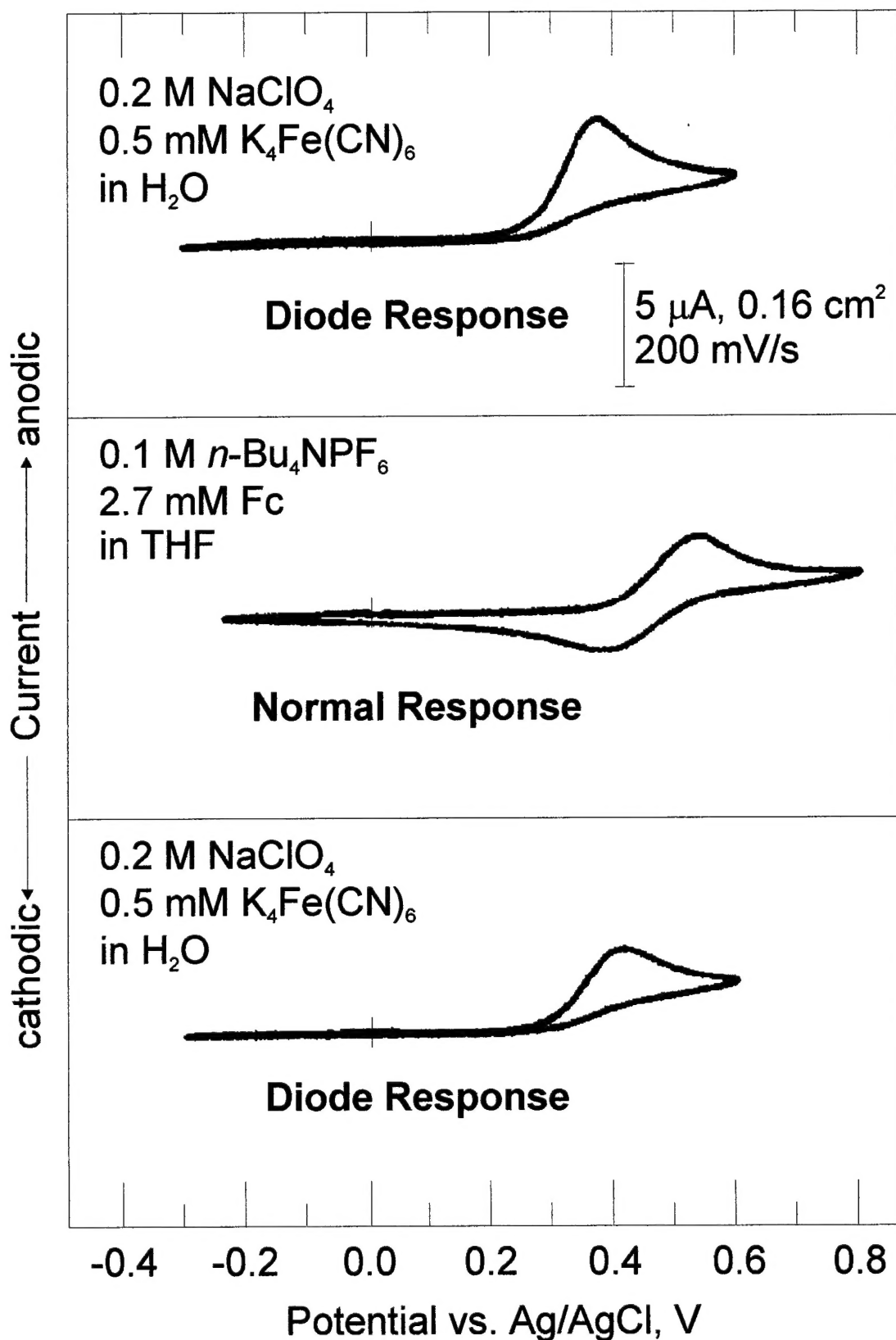
# A SAM-Based Photoswitchable Molecular Diode



## Basis for a Photoswitchable Diode

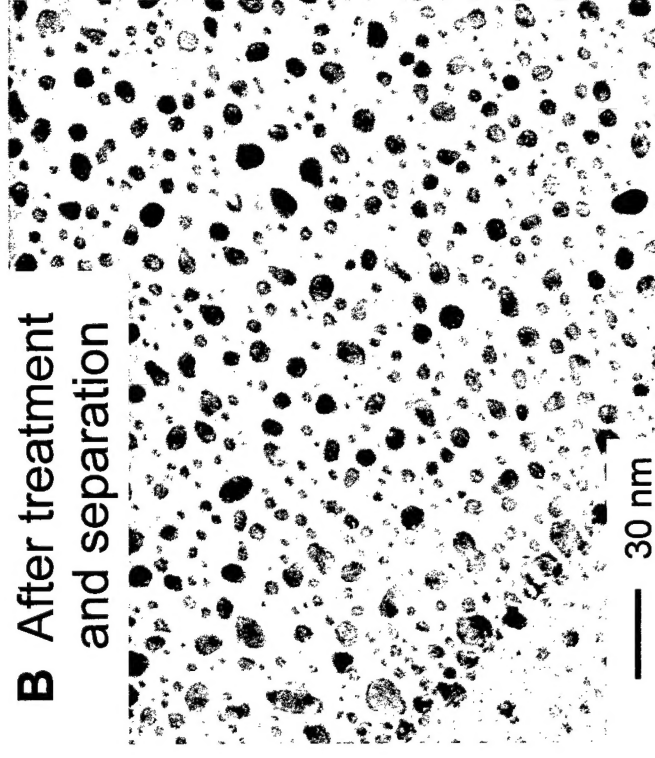
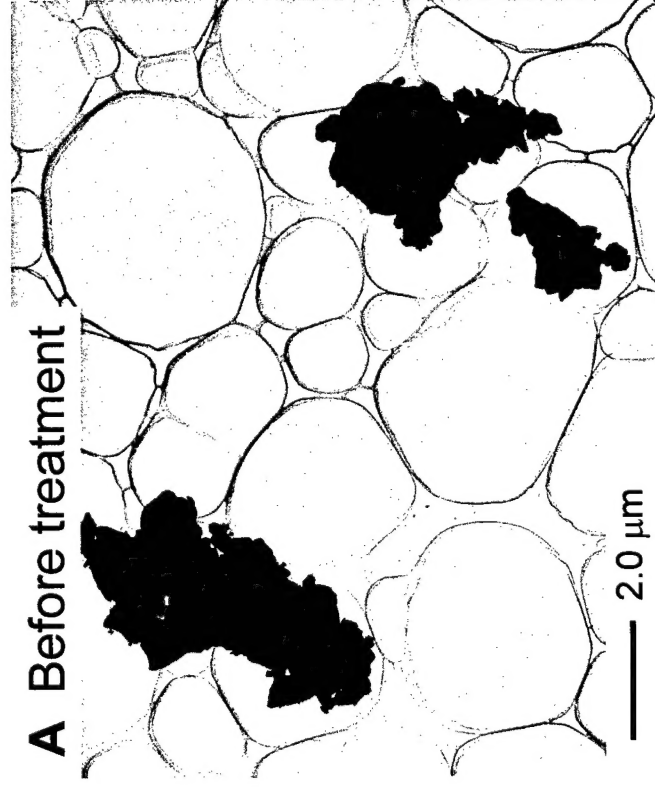


# Solvent Dependent Diode-Like Behavior





# HTSC Nanoparticles by “Whittling” Away $\text{YBa}_2\text{Cu}_3\text{O}_7$ Superconducting Powders

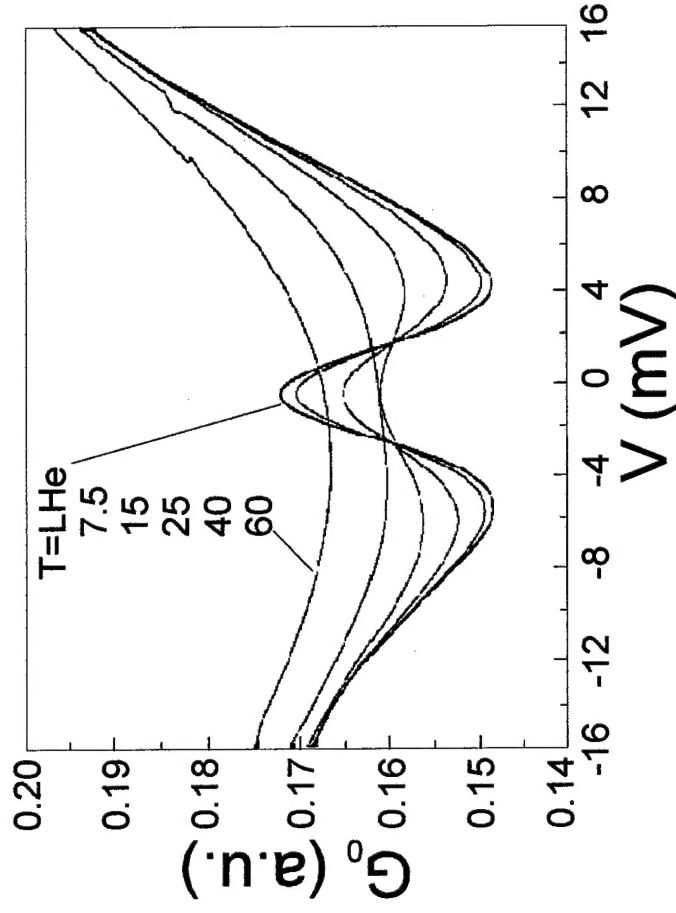
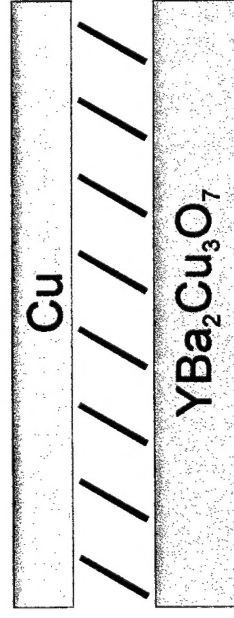


$\text{YBa}_2\text{Cu}_3\text{O}_7$  Powder

Nanoparticles

1. Ethylenediamine/  
sonication
2. Separation

# SIN Tunnel Junction Formed from a SAM of Diaminododecane



L. Greene, C. A. Mirkin, and coworkers